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**Binary Phase Diagram Series: 1,3,3-Trinitroazetidine  
(TNAZ)/2,4,6-Trinitrotoluene (TNT)**

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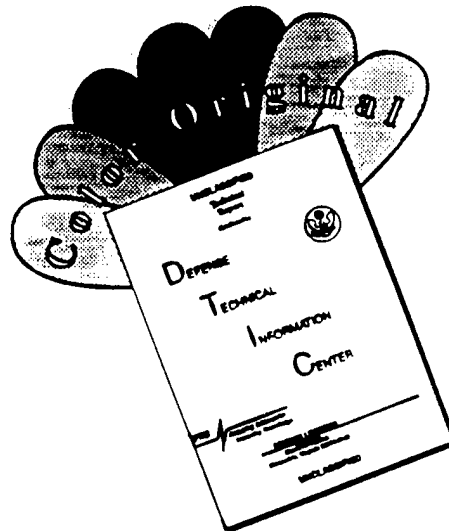
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## PREFACE

This report was prepared by the Wright Laboratory/Armament Directorate, Munitions Division, Energetic Materials Branch (WL/MNME), Eglin Air Force Base, Florida 32542-5910, and covers work performed during the period from August 1996 to January 1997. Robert L. McKenney, Jr. (MNME) managed the program for the Directorate.

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## SECTION I

### INTRODUCTION

#### 1. BACKGROUND

1,3,3-Trinitroazetidine (**TNAZ**), a novel high performance energetic material of considerable interest to the DoD, was first prepared by Archibald and co-workers in 1990 (Reference 1). While **TNAZ** is a powerful and thermally stable energetic material, its application to melt cast energetic formulations has been limited by its high volatility characteristics and its tendency to form low density castings at atmospheric pressure (Reference 2). In an attempt to ameliorate these unacceptable characteristics, researchers at this laboratory are endeavoring to form binary eutectic compositions with a variety of other energetic materials (References 3, 4, 5 and 6). Binary mixtures with pentaerythritol tetranitrate (**PETN**), 2,4,6-trinitrotoluene (**TNT**) and 1,3,5-trinitrobenzene (**TNB**) have been characterized with respect to performance and sensitivity (References 3, 4 and 5). During the course of one of the previous investigations (Reference 6) it was demonstrated that **TNAZ** exists in at least two polymorphic forms, one stable at ambient temperature (**TNAZ I**) and one unstable (**TNAZ II**), and that the former is more dense than the latter. The density increase that occurs with the spontaneous transition from **TNAZ II** to **TNAZ I** is believed to be the primary cause of low density castings with neat **TNAZ**. It has also been reported (Reference 7) and shown during this investigation that **TNT** exists in more than one polymorph. The objective of this effort is to experimentally characterize the **TNAZ/TNT** binary eutectic system by differential scanning calorimetry (DSC) and hot stage microscopy (HSM).

## SECTION II

### EXPERIMENTAL

#### 1. PHASE DIAGRAM CALCULATION

The eutectic composition and melting temperature for this two component system, **TNAZ/TNT**, were calculated using a computer program in BASIC (Reference 8). The program iteratively solves equation (1) using heats of fusion and melting points from both components as input data,

$$R \ln x = \Delta H_{\text{fus}}(-1/T + 1/T_o) \quad (1)$$

where  $T$  is the melting point (degrees K) of the eutectic composition and  $T_o$ ,  $\Delta H_{\text{fus}}$  and  $x$  are the melting point, heat of fusion and mol fraction of component A or B, respectively, and  $R$  is the gas constant (1.987 calories degree  $K^{-1} \text{mol}^{-1}$ ). Melting points and heats of fusion used for phase diagram calculations were experimentally determined by DSC operations with the stable polymorphic forms of both components. While the BASIC program provides the composition and melting point of the eutectic mixture, it does not provide a usable graphical presentation or corresponding list of associated liquidus temperatures. These temperatures were obtained by solving equation (1) for each component at selected mol fraction values. The mol percent and temperature values used to calculate the phase diagram for the above system are shown in Table 1.

#### 2. THERMAL CHARACTERIZATION

##### a. Differential Scanning Calorimetry (DSC)

**TNT** and selected **TNAZ/TNT** mixtures were thermally characterized by using a TA Instruments, Dual Differential Scanning Calorimeter, Model 912, equipped with a 2100 Thermal Analyzer Data System. Standard aluminum sample pans and lids, TA Instruments Part Nos. 072492 and 073191, were used for all melting operations carried out by using the standard Dual Sample DSC (DSDSC) cell. Lids were inverted to minimize free volume over the sample. An upper temperature limit of 105 °C and sample weights not exceeding 4 mg were used throughout this investigation to minimize the chance for leakage from the sample pans.

Melting operations were also carried out by using a Pressure DSDSC cell that was pressurized to 2.76 MPa (400 psig). Standard aluminum sample pans and lids were used for these melting operations with lids not inverted, but perforated with one pin hole. A minimum of two melting operations were carried out for all materials at a heating rate of

5 °C/min. Cooling operations for experiments carried out at 101.2 KPa were accomplished at 5 °C/min by using ice/water as a cooling medium. Mixtures were prepared by grinding weighed portions of dry energetic material in an agate mortar with a glass pestle to ensure homogeneity. The instrument was calibrated by using indium metal as a temperature standard. Endothermic and exothermic peak temperatures are reported for all heating and cooling operations.

b. Hot Stage Microscopy (HSM)

HSM experiments were carried out by using a Mettler hot stage, Model FP 82, equipped with an FP 80 Central Processor. All observations were made with a Leitz Orthoplan Universal Largefield microscope equipped with a polarizing condenser and high-resolution video system, Javelin Smart Camera, Model JE3762DSP, which was operated at shutter speeds of 1/250 or 1/500 s. The video system is also equipped with a FOR-A video timer, Model VTG-55. All photomicrographs were obtained through a Leitz NPL 10X 0.20P lens (150x). Heating and cooling rates were 5 °C/min unless otherwise specified. Below approximately 45 °C the cooling rate was not controlled.

3. ENERGETIC COMPONENTS

a. TNT

TNT was recrystallized in a single operation from cyclohexanone and dried under vacuum.

b. TNAZ

TNAZ was purified by crash-precipitating from an ethanol solution into a mixture of ice and water.

## SECTION III

### RESULTS

#### 1. THERMAL CHARACTERIZATION

##### a. Thermal Properties of TNT and TNAZ

The melting point and heat of fusion obtained by DSC operations at 101.3 KPa for TNT were  $81.0 \pm 0.1$  °C and  $5.087 \pm 0.077$  kcal/mol, respectively [lit. mp 80.6 to 81.5 °C and  $\Delta H_{\text{fus}}$  4.585 to 5.403 kcal/mol (References 7a and b)]. The average melting point and heat of fusion for TNT from initial heating operations at 2.76 MPa were  $81.7 \pm 0.1$  °C and  $6.029 \pm 0.020$  kcal/mol, respectively. The experimental melting point and heat of fusion obtained for TNAZ were 100.8 °C and  $6.714 \pm 0.115$  kcal/mol, respectively [lit. mp 101.1 °C/6.405 kcal/mol (Reference 6)]. The TNT melting and recrystallization characteristics were also observed by HSM operations. Melting occurred over the temperature range 79.7-81.6 °C with significant premelt darkening. After complete melting and supercooling to less than 36.7 °C it recrystallized with an almost formless front and characteristic grainy structure as shown in Figure 1. Recrystallization at approximately 75 °C in the presence of seed crystals yielded evidence of polymorphism as described in McCrone (Reference 9) and shown in Figure 2, where one crystal front grows into the other. Polymorphism was also observed by DSC operations on quench-recrystallized TNT as described in Reference 7c and d. TNAZ was previously shown to exist in at least two polymorphic forms (Reference 6).

##### b. DSC Characterization of TNAZ/TNT Mixtures

The initial melting operations with seventeen freshly ground mixtures of TNAZ and TNT yielded a consistent, endothermic event at an average temperature of  $60.6 \pm 0.04$  °C that is caused by eutectic melting. A second endothermic event that is attributed to the dissolution of the TNAZ or TNT component into the liquid eutectic composition was observed for all of the mixtures except that containing 38.5 mol percent TNAZ. Remeasurements of these endothermic events with samples obtained by freezing of the initial melts resulted in a shift of the eutectic endothermic events to the temperature range of 58.2 - 59.9 °C (average  $59.1 \pm 0.2$  °C) with the higher temperatures occurring around the eutectic composition and the lower closer to the pure components. Remelting operations carried out on three of the fused mixtures containing 11.6, 34.2 and 44.1 mol percent TNAZ that had been re-ground resulted in eutectic melting temperatures of 58.1, 59.9 and 60.0 °C, which were consistent with the temperatures obtained from the operations on the fused mixtures. The temperature values for the dissolution of the TNT component into the eutectic liquid were slightly lower than the calculated values, but remained essentially constant for all melting operations on a specific mixture. The experimental TNAZ liquidus

temperatures fell predominately below the calculated liquidus curve. The data from all DSC operations on these mixtures are shown in Table 2. All of the mixtures are affected by supercooling, with those around the eutectic composition often standing at room temperature for considerable periods of time before crystallization occurs. Recrystallization events for mixtures rich in either component are typically composed of two exothermic events, the initial event, component recrystallization, generally being sharp and the second event, eutectic recrystallization, being broad.

#### c. Calculated Phase Diagram

The calculated melting point and mol percentage value for the **TNAZ** component in the eutectic composition are 61.4 °C and 34.5, respectively. The calculated phase diagram along with experimental data from DSC and HSM operations is shown in Figure 3.

#### d. HSM Characterization of **TNAZ**/TNT Mixtures (Mol Percent)

(1) **TNAZ**/TNT Mixture (81.6/18.4) - Melting was first observed in the range 58.5-59.5 °C (eutectic composition) and then at 93.4 °C (**TNAZ** component). Cooling operations produced three events, liquid to solid crystallization followed by a solid to solid transition where the overall thin crystalline film lightened and then by another crystal front moving from bottom to top resulting in an overall darkening of the matrix (Figure 4). All solids in this sequence of events are dendritic in appearance. Preceding the appearance of the final crystal front dark areas were formed that had the appearance of liquid being expelled from the solid matrix. It is believed the first two events correspond to the recrystallization of **TNAZ** followed by the spontaneous transition to another **TNAZ** polymorph. This transition process is possibly **TNAZ II** converting to **TNAZ I** (Reference 6). The third front is believed to be the recrystallization of the eutectic composition.

(2) **TNAZ**/TNT Mixture (54.2/45.8) - The eutectic composition melted at 61.4 °C and **TNAZ** at 82.6 °C. Upon cooling, a double recrystallization occurred at 37.2 °C. The first crystals to appear were long dendrites that were then covered by a darker dendritic structure. Remelting of the darker eutectic composition left a thin layer of solid **TNAZ** with a characteristic dendritic structure similar to the initial crystals observed during the initial recrystallization (Figure 5). Cooling yielded crystallization at 39.2 °C that occurred with a continuous, almost formless front that was interlaced with needle-like crystals moving parallel to the front. This was followed at 31.9 °C by another continuous front that darkened the basic structure. The event is shown in (Figure 6).

(3) **TNAZ**/TNT Mixture (44.1/55.9) - The eutectic composition melted at 61.4 and **TNAZ** at 67.7 °C. This composition supercooled to 14 °C without crystallization then, upon warming, crystallized in the range 26-28 °C with a continuous needle-like front. The surface

darkened immediately behind the crystal front as it progressed across the field-of-view (Figure 7).

(4) **TNAZ/TNT Mixture (39.3/60.7)** - The melting point of the eutectic composition and of **TNAZ** was 60.0 and 64.1 °C, respectively. This mixture supercooled to below 30 °C then recrystallized with a continuous, needle-like front (Figure 8) followed by surface roughening and darkening immediately behind the front. The latter is believed to be crystallization of the eutectic composition.

(5) **TNAZ/TNT Mixture (38.5/61.5)** - The mixture melted over the temperature range 58.7-62.9 °C. Recrystallization occurred initially as bundles of long, flattened needles at 44 °C (Figure 9a and b) followed by the appearance of islands of a grainy material at about 40 °C (Figure 9c).

(6) **TNAZ/TNT Mixture (34.2/65.8)** - Eutectic melting occurred at 60.9 °C and **TNT** at 63.7 °C. Cooling was characterized by extreme supercooling with crystallization occurring at approximately 14 °C. The characteristics of the angular crystal front and time-related surface texture changes are shown in Figure 10. The surface darkened and the texture appeared to roughen during the approximate two-minute period following the passing of the crystal front from the field-of-view.

(7) **TNAZ/TNT Mixture (11.6/88.4)** - The eutectic composition melted at 61.4 and **TNT** at 78.9 °C. The cooling operation resulted in supercooling to approximately 27 °C after which recrystallization occurred with a continuous front (**TNT**) that was followed by a second front with surface darkening and roughening (Figure 11).

All HSM operations with mixtures are summarized in Table 3.

#### e. **TNAZ/TNT Mixed Fusion**

A mixed fusion slide was prepared by a modification of the method described in McCrone (Reference 9) and is shown in Figure 12. **TNAZ** was applied to the slide first with coverslip. **TNT** was then melted and allowed to wick under the coverslip until contact was made with the solidified **TNAZ**. The vertical contact line between **TNT** (left) and **TNAZ** (right) extends from top center to the bottom slightly to the left of center. It is sandwiched between a wide zone of mixing characterized by multi-colored plates oriented in a horizontal direction on the **TNT**-rich side and an area of fine particles on the side rich in **TNAZ**. Characteristic **TNT** and **TNAZ** thin film structures are seen on the far left and far right, respectively. Eutectic melting occurred rapidly at the point of contact (Figure 13) over the range 59.4-61.0 °C and continued slowly until **TNT** and **TNAZ** had completely melted at 80.7 and 99.8 °C, respectively. Movement and color changes were observed in the zone of

mixing on the **TNT** side of the eutectic at 57.3 °C and in the greenish area in the **TNAZ** solid (upper right corner of Figure 12) at 57.8 °C. Upon cooling, **TNAZ II** recrystallized at 52.7 °C with a continuous, formless front (Figure 14a), then spontaneously converted to **TNAZ I** (Figure 14b) and continued to grow rapidly into the zone of mixing as large, well-defined platelet-like crystals (Figure 14c). The growth rate of these platelets slowed rapidly in the area of the eutectic mixture. **TNT** recrystallized at 32.9 °C with a continuous, formless front. The continuous **TNT** front moved rapidly through the **TNT** melt (Figure 15a), across the eutectic area and large **TNAZ** platelets (Figure 15b) and finally across the entire **TNAZ** section of the slide. The continuous front is shown just entering the **TNAZ** area immediately behind the platelets in Figure 15c.



## SECTION IV

### DISCUSSION

Evidence of polymorphism was observed by DSC operations on neat, solvent-recrystallized and on quench-cooled TNT at 101.3 KPa. The polymorph obtained by quench-cooling melted 1.1 °C lower than the polymorph obtained by recrystallization. The amount of lower melting polymorph was just detectable in the solvent-recrystallized TNT, whereas it made up a significant portion of the quench-cooled material. The experimental melting point and heat of fusion used for all calculations during this investigation were obtained by DSC operations on solvent-recrystallized TNT and were consistent with literature values. Polymorphism was also observed by HSM operations where TNT, recrystallized from the melt at approximately 75 °C in the presence of seed crystals, yielded plate-like crystals that grew into and through one another. Neat TNAZ, as described in Reference 6, is also affected by polymorphism during recrystallization operations.

The experimental TNAZ liquidus temperatures obtained by DSC heating operations with both freshly ground and fused mixtures form a continuous, convex-shaped curve positioned below the calculated liquidus curve. A best-fit curve through the experimental liquidus temperatures showed they originated from a TNAZ melting temperature of 100.1 °C, which is consistent with the experimental melting temperature of pure TNAZ I. The experimental TNT liquidus temperatures, while more in agreement with those calculated by using equation (1), fall slightly below those calculated. Again a best-fit analysis of the four data points show they originate from a melting temperature of 81.4 °C, a value consistent with that of solvent-recrystallized TNT. The average melting temperature for the eutectic composition from initial DSC melting operations (60.6 °C) agrees well with the calculated value (61.4 °C), while that from remelting operations is shifted to a lower average temperature (59.1 °C). This latter melting process actually varied between 58.2 and 60.0 °C with the higher values occurring in the TNAZ mol fraction range of 0.342 to 0.502. It was demonstrated that this melting point shift was not the result of operating on fused versus freshly ground mixtures.

Equation (1), solved over the TNT mol fraction range of 0.953 to 0.658 for consistent heats of fusion, yielded an average value of  $4.944 \pm 0.107$  kcal/mol. A similar operation for TNAZ, carried out over the mol fraction range of 0.983 to 0.385, did not yield consistent values. As a consequence, a calculation was then carried out by using equation (2)

$$\text{mol fraction}_{\text{TNT}}(4944) + \text{mol fraction}_{\text{TNAZ}}(x) = \text{measured } \Delta H_{\text{fus}} (\text{initial}) \quad (2)$$

substituted with mixture heats of fusion from initial melting operations. Two TNAZ mol

fraction ranges, 0.983-0.780 and 0.687-0.235, yielded consistent sets of heats of fusion with average values of  $6.299 \pm 0.032$  and  $5.847 \pm 0.259$  kcal/mol, respectively. This calculation was repeated by using mixture heats of fusion from remelting operations. Again, two sets of consistent heats of fusion were obtained with average values of  $6.286 \pm 0.106$  and  $5.406 \pm 0.080$  kcal/mol. The **TNAZ** mol fraction ranges associated with these average values are 0.983-0.840, 0.687 and 0.816, 0.780, 0.639-0.235, respectively. Finally, energy combinations of 4.944/6.299, 4.944/5.847 and 4.944/5.406 kcal/mol coupled with a temperature combination of 81.0/100.3 °C were substituted into the eutectic computer program. These operations yielded eutectic mol fraction (**TNAZ**)/melting point combinations of 0.358/60.0, 0.374/58.9 and 0.391/57.6 °C, respectively. The first two combinations are consistent with the average experimental eutectic melting points from the initial and remelting operations, 60.6 and 59.1 °C, respectively, and with the estimated eutectic composition range of 0.385 to 0.342 mol fraction **TNAZ** from experimental data.

The interpretations of the overall findings are described below:

- a. Both **TNAZ** and **TNT** exhibit the characteristics associated with polymorphism when combined.
- b. The transition from their starting polymorphs is initiated after the eutectic composition melts during the initial melting operation. This implies the eutectic melting point will be at or close to the calculated value based on the properties obtained from pure components and that the eutectic melting point will reflect these polymorph changes only with remelting operations. It also implies the component liquidus curves from the initial melting operations will deviate from those calculated.
- c. **TNT** is assumed to have transitioned completely to another polymorph.
- d. The findings relative to **TNAZ**, while less clear, suggest that **TNAZ** is in a polymorphic transition state or exists in more than the two polymorphic forms previously observed.

## SECTION V

### CONCLUSIONS

The binary phase diagram for the **TNAZ/TNT** system has been predicted computationally by using the measured heats of fusion and melting points associated with the individual components. Experimentally, it has been demonstrated that mixtures of **TNAZ** and **TNT** exhibit the thermal characteristics associated with a simple binary eutectic system affected by polymorphism that is attributed to both components.

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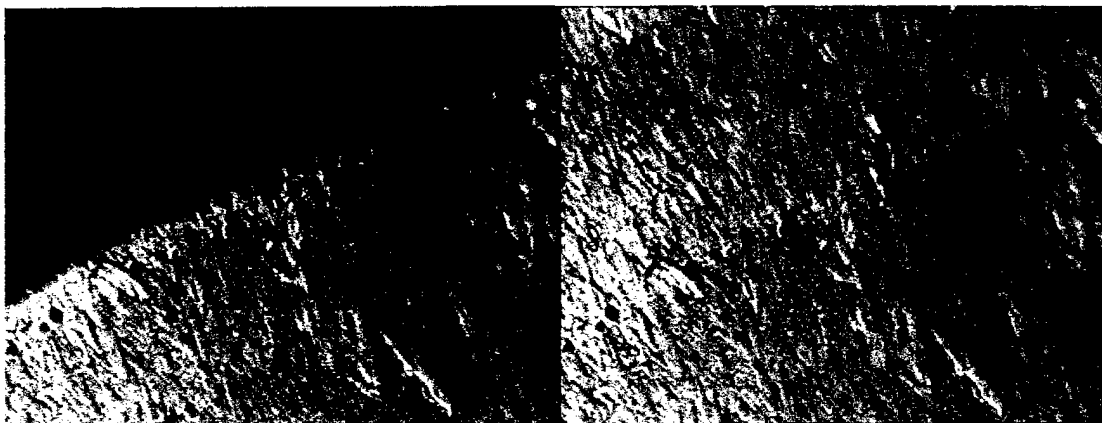


Figure 1. Thin film of TNT crystallizing at 36.7 °C



Figure 2. Thin crystalline film of TNT recrystallized at 75 °C in the presence of seed crystals

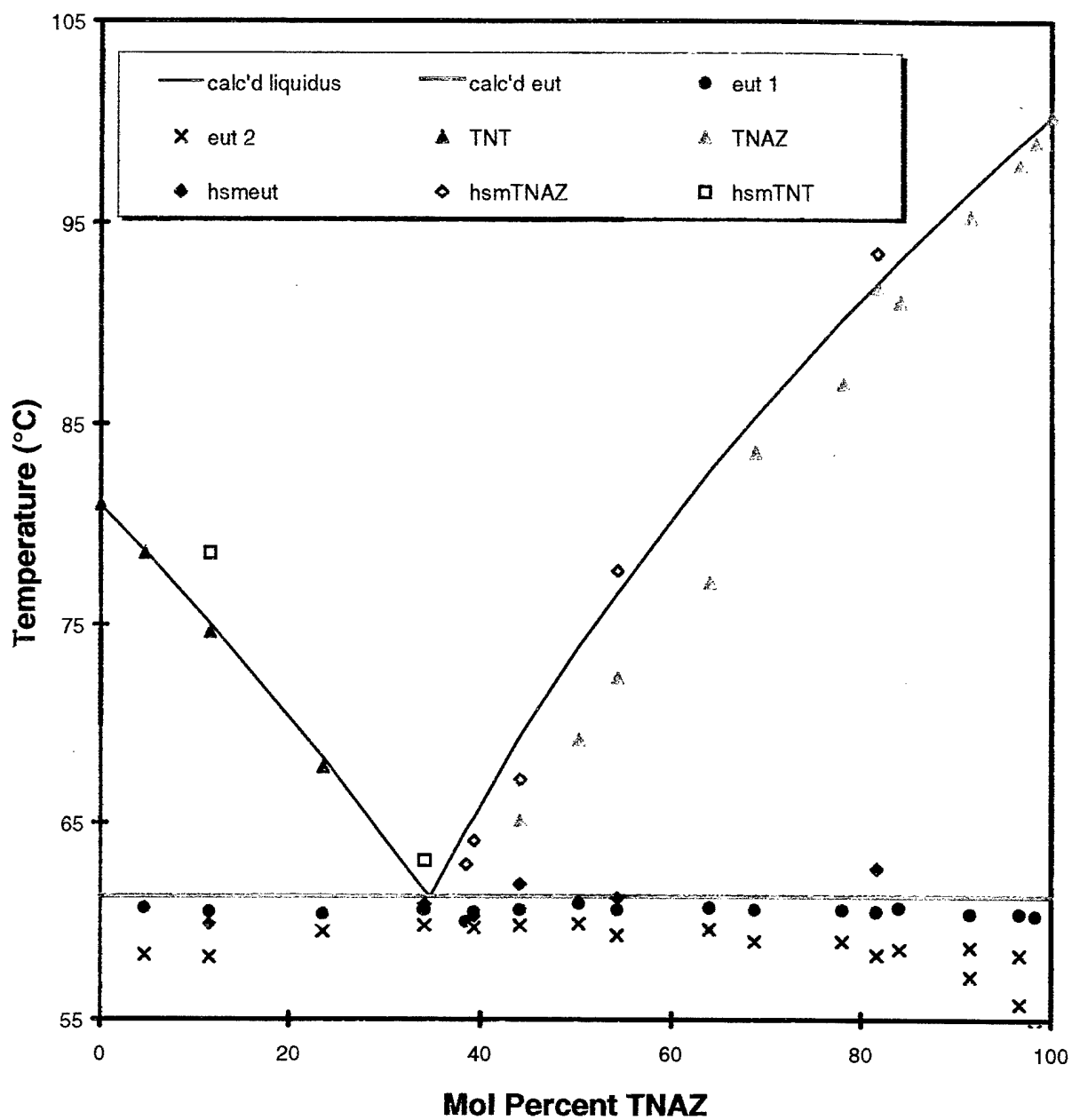


Figure 3. Calculated phase diagram for the TNAZ/TNT system with supporting experimental data

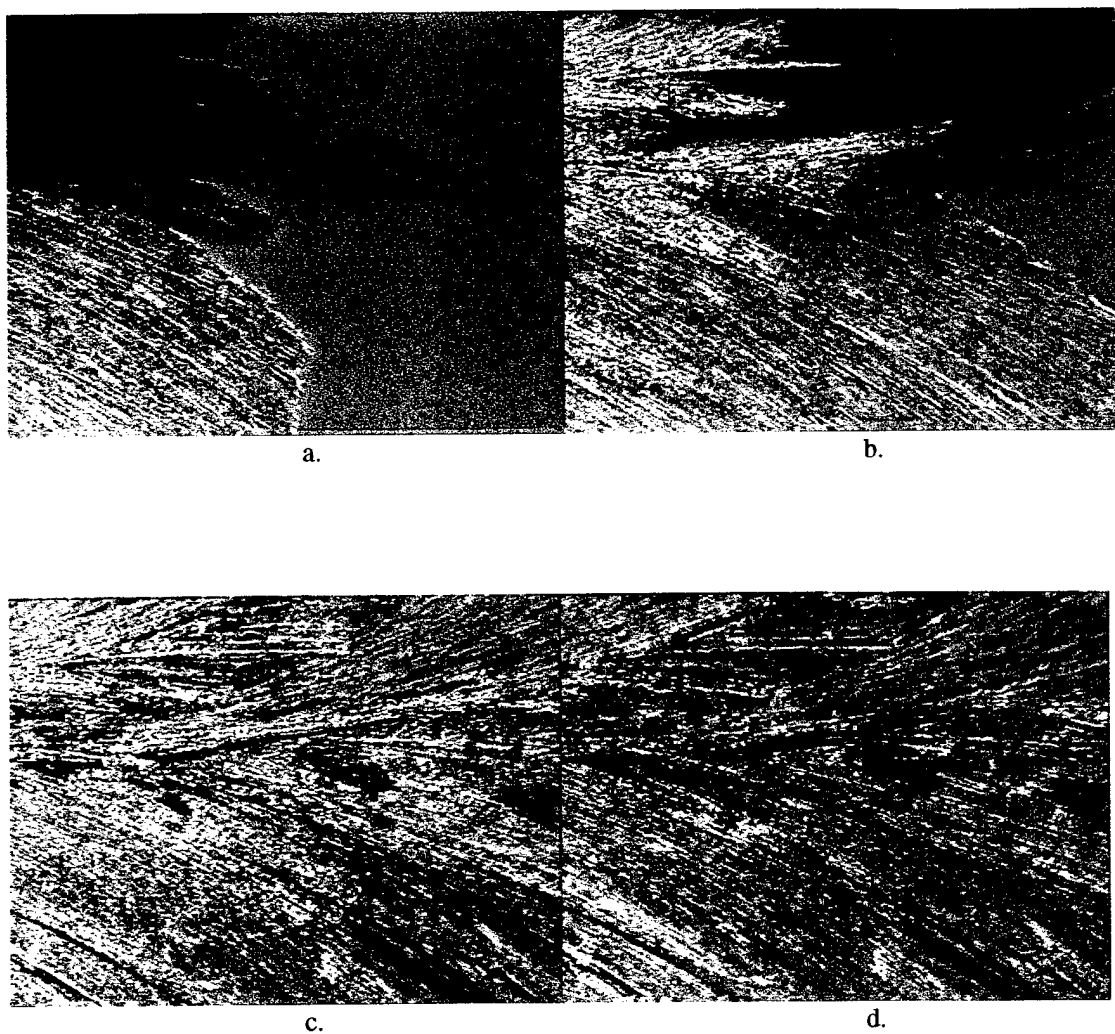
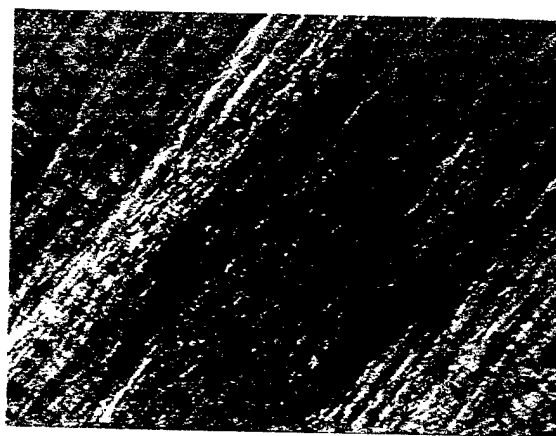
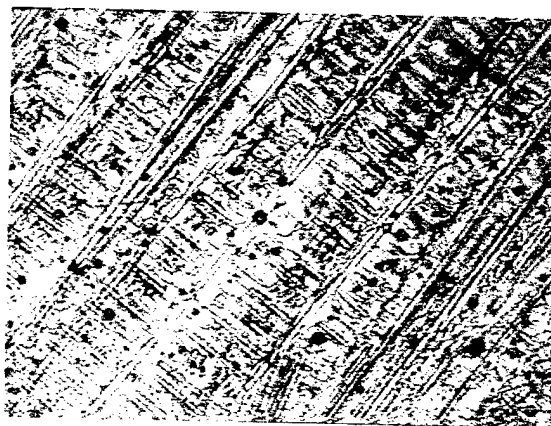


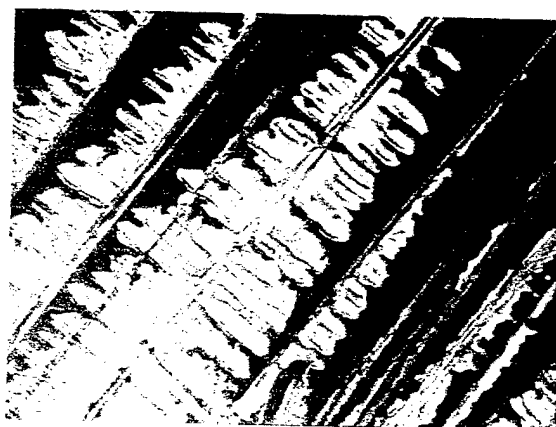
Figure 4. Recrystallization of a mixture containing 81.6 mol percent TNAZ, (a) initial unstable TNAZ polymorph, (b) transition to stable TNAZ polymorph, (c) recrystallization of eutectic and (d) final thin crystalline film



a.



b.



c.

Figure 5. Photomicrographs of TNAZ/TNT (54.2/45.8 mol percent) mixture:  
 (a) Eutectic composition at 25 °C, (b) Dendritic TNAZ layer after  
 melting eutectic composition at 61.8 °C, (c) TNAZ melting



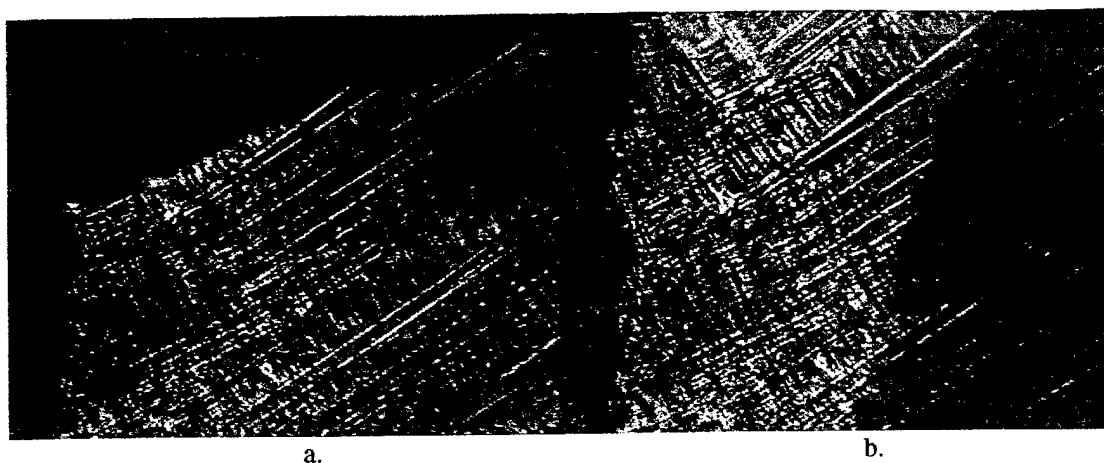


Figure 6. Recrystallization of a mixture containing 54.2 mol percent TNAZ: (a) TNAZ crystallization and (b) eutectic crystallization at 31.0 °C (dark front moving from right to left)

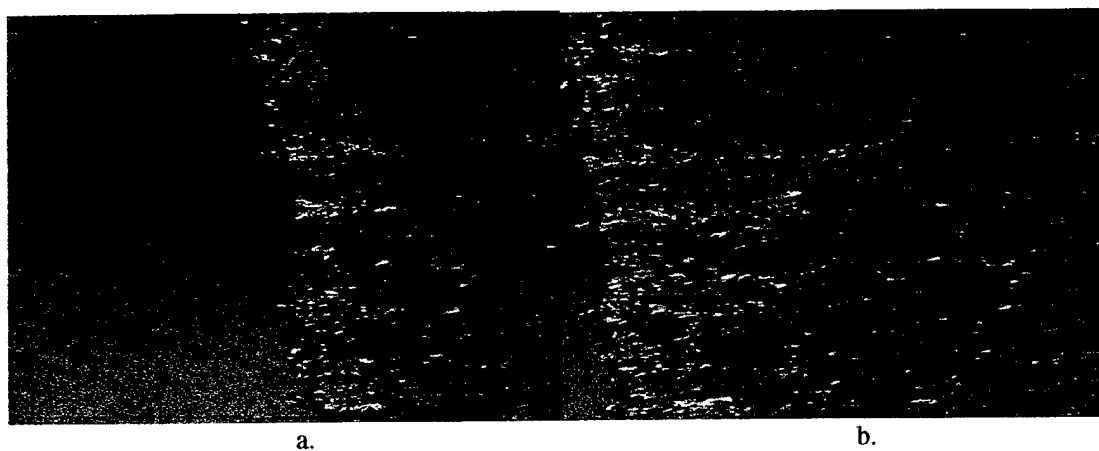


Figure 7. (a) Mixture containing 44.1 mol percent TNAZ recrystallization at 28.5 °C as a light leading edge, (b) followed by immediate darkening

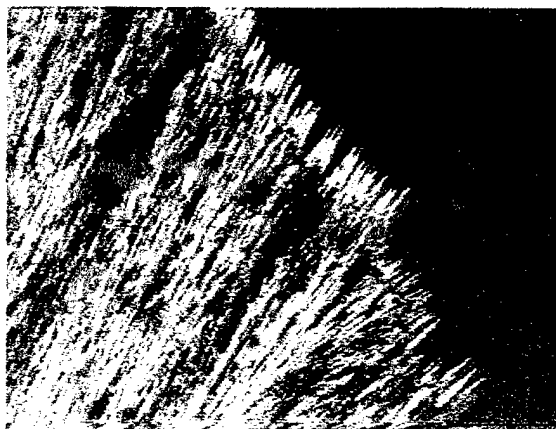


Figure 8. Mixture containing 39.3 mol percent TNAZ recrystallizing at 29 °C as an apparent single-event process with a needle-like front

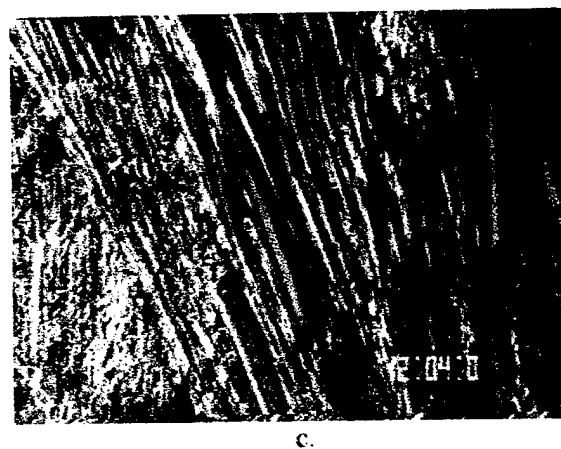
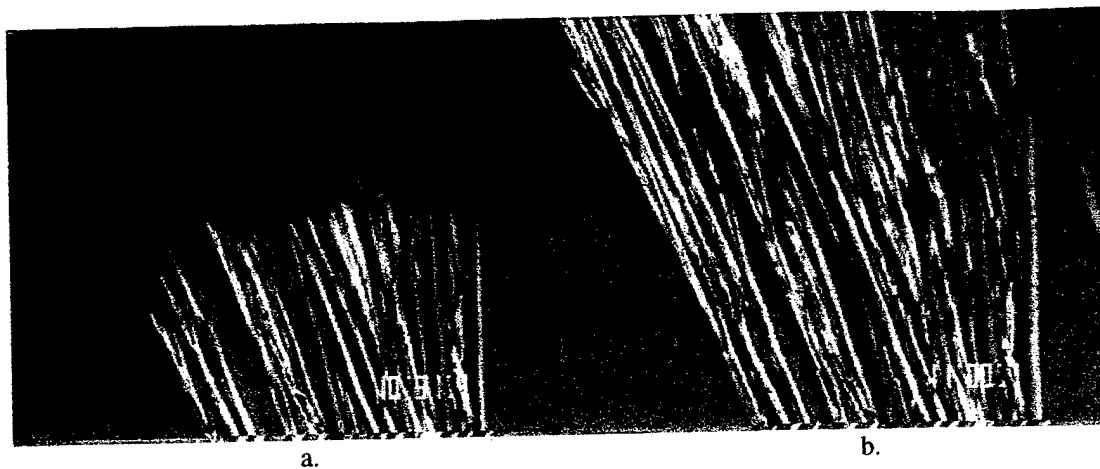


Figure 9. Mixture containing 38.5 mol percent TNAZ recrystallizing at 44 °C as (a) and (b) long, flattened bundles of needles and (c) at 40 °C as patches of grainy material



Figure 10. Mixture containing 34.2 mol percent **TNAZ** recrystallizing at approximately 14 °C exhibiting a time-related surface texture change/darkening

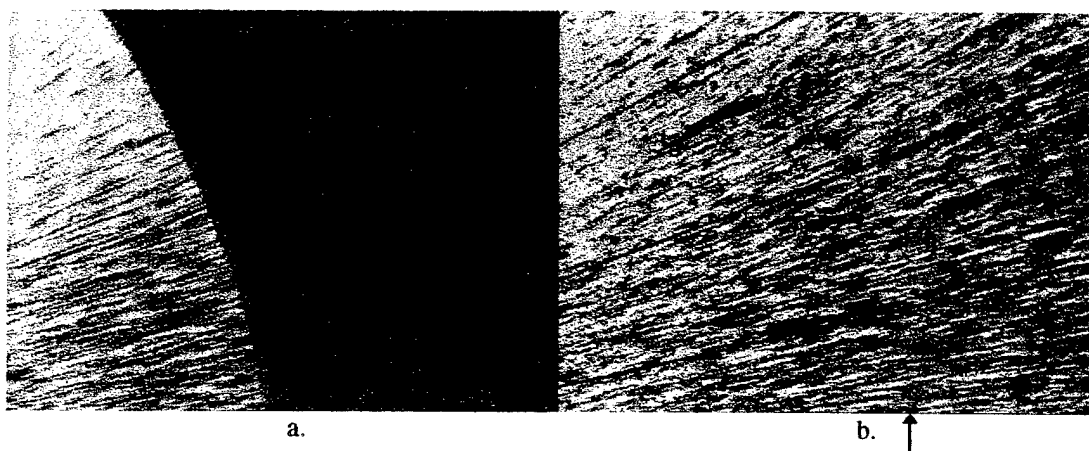


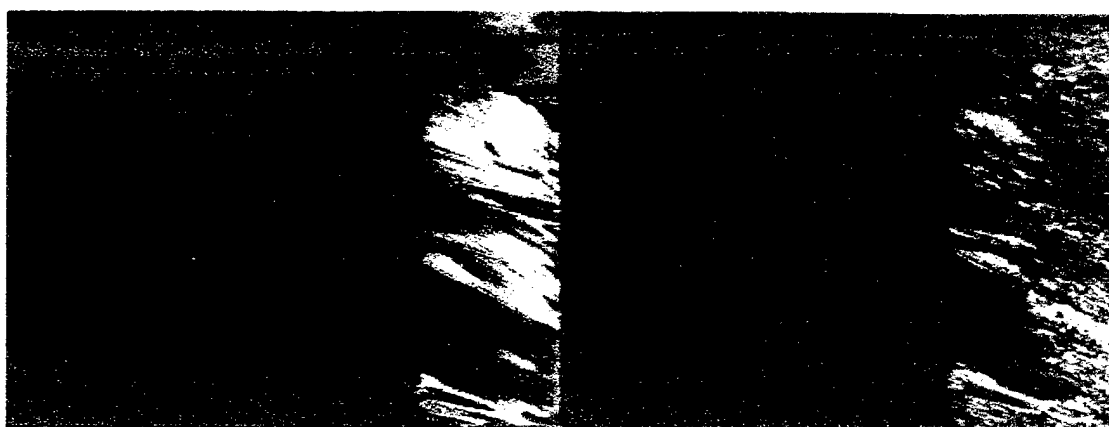
Figure 11. Mixture containing 11.6 mol percent **TNAZ** recrystallizing at 27 °C (a) a formless **TNT** crystal front and (b) eutectic composition recrystallizing over **TNT** (arrow indicates recrystallizing front)



Figure 12. Mixed fusion type thin crystalline film of TNT (left) and TNAZ (right)



Figure 13. TNAZ/TNT mixed fusion thin crystalline film showing eutectic melting in the temperature 59.4 - 61.6 °C



a

b.



c.

Figure 14. Mixed fusion thin crystalline film: (a) TNAZ polymorph (believed to be TNAZ II) recrystallizing at 52 °C, (b) TNAZ II spontaneously transitioning to another polymorph (believed to be TNAZ I) and (c) TNAZ crystals growing into the zone of mixing

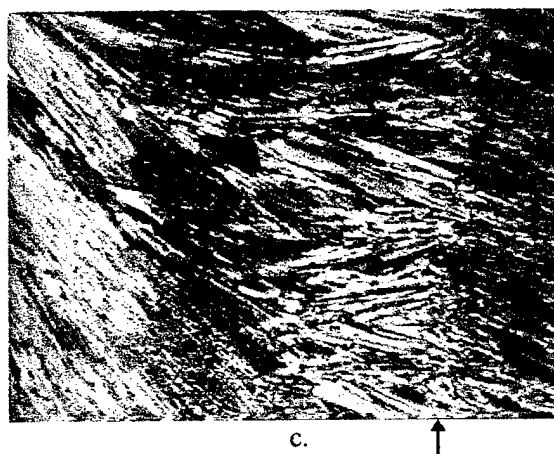
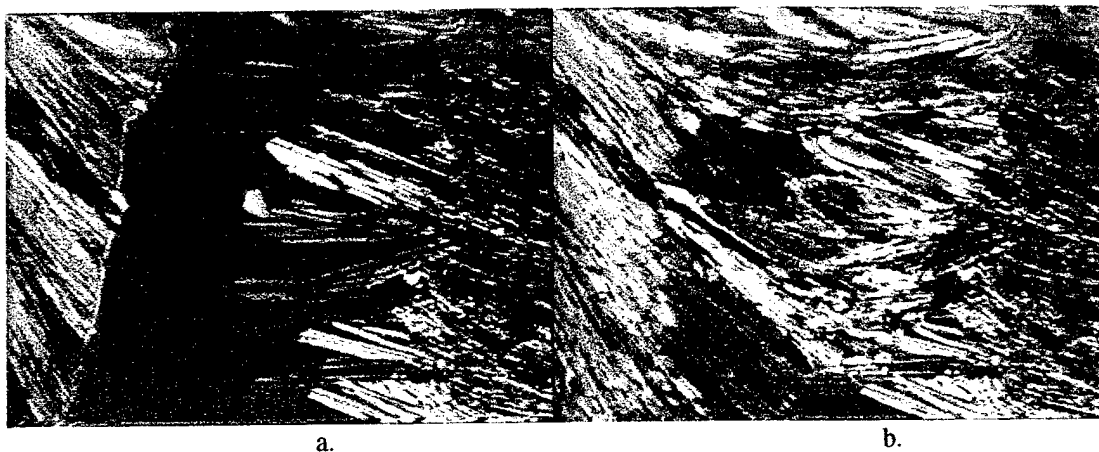


Figure 15. Mixed fusion thin crystalline film: (a) TNT recrystallizing at 32.9 °C with a formless front, (b) front crossing over TNAZ crystals and (c) front beginning to cross over main TNAZ thin film (arrow)

Table 1. Mol Percent/Calculated Temperatures for the TNAZ/TNT Phase Diagram

Mol Percent <u>TNAZ</u>	Temperature <u>(°C)</u>
0	81.0
4.7	78.7
11.6	75.1
23.5	68.3
34.2	61.6
34.5 <sup>1</sup>	61.4 <sup>2</sup>
38.9	65.4
44.1	69.7
54.2	77.1
68.7	85.9
81.6	92.6
96.6	99.4
100.0	100.8

1. Eutectic composition.
2. Eutectic temperature.



Table 2. Endothermic Peak Temperatures for All DSC Melting Operations with  
TNAZ/TNT Mixtures

<u>Mol Percent</u> <u>TNAZ</u>	<u>Temperature (°C)</u>			<u>TNT</u>	<u>TNAZ</u>
	<u>Eutectic (1)</u>	<u>Eutectic (2)</u>	<u>Eut (2) reground</u>		
98.3	60.3	54.5			99.0
96.6	60.4	55.8/58.3			97.9
91.4	60.4	57.2/58.7			95.3
84.0	60.7	58.6			91.1
81.6	60.5	58.3			91.8
78.0	60.6	59.0			87.0
68.7	60.6	59.0			83.6
63.9	60.7	59.6			77.1
54.2	60.6	59.3			72.3
50.2	60.9	59.9			69.2
44.1	60.6	59.8	60.0		65.1
39.3	60.5	59.7			62.0
38.5	61.0	60.0			
34.2	60.6	59.8	59.9	62.1	
23.5	60.4	59.5		67.8	
11.6	60.5	58.2	58.1	74.6	
04.7	60.7	58.3		78.6	

1 Initial melting operation.

2 Remelting operation.

Table 3. TNAZ/TNT Data from All HSM Operations

Mol Percent <u>TNAZ</u>	<u>Temperature (°C) (Initial/Remelt)</u>		
	<u>Eutectic</u>	<u>TNT</u>	<u>TNAZ</u>
81.6	59.5		93.4
54.2	61.4		82.6
44.1	61.4		67.7
39.3	60.0		64.1
38.5	62.9		
34.2	60.9	63.7	
11.6	61.4	78.9	
Mixed Fusion	60.6		

Table 4. Calculated/Measured Heats of Fusion

Mol Fraction <u>TNAZ</u>	<u>Experimental</u> <u>Initial/Remelt</u>	<u>Calculated</u>		
		<u>TNT<sup>1</sup></u>	<u>TNAZ<sup>2</sup></u>	<u>TNAZ<sup>3</sup></u>
0.983	6393/6155		6418	6176
0.966	6198/6047		6242	6086
0.914	6161/6101		6276	6210
0.840	6086/5793		6304	6696
0.816	5080/4929			5532
0.780	5966/5386		6254	5511
0.687	5622/5851		5931	6264
0.639	5454/5384		5742	5633
0.542	5342/5350		5678	5693
0.502	5303/5144		5659	5342
0.441	5464/5276		6123	5697
0.393	5306/5033		5865	5170
0.385	5096/4937			4926
0.342	5277/5083	5226	5918	5350
0.235	5229/5006	4870		5208
0.116	5032/4911	4716		
0.047	5048/4750	4966		

1. Average TNT heat of fusion:  $4.944 \pm 0.107$  kcal/mol (0.047-0.342).
2. Average TNAZ heats of fusion from initial melting operations:  $6.299 \pm 32$  (0.780-0.983),  $5.847 \pm 0.259$  (0.235-0.687) kcal/mol.
3. Average TNAZ heats of fusion from remelting operations:  $6.286 \pm 0.106$  (0.687, 0.840-0.983),  $5.406 \pm 0.080$  (0.235-0.639, 0.780, 0.816) kcal/mol.

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